NBIT Final Report for AOARD Grant FA2386-10-1-4072

"**Meso size effect (MSE) from self-assembled carbon structures and their device applications**"

23 August 2013

Name of Principal Investigators (PI and Co-PIs):

	Jiwoong Park (US)	**Hee Cheul Choi (Korea)**
– e-mail address :	jpark@cornell.edu	choihc@postech.edu
– Institution :	Cornell University	POSTECH
– Mailing Address :	Baker Laboratory, Ithaca NY 14853 USA	San 31, Hyoja-dong, Namgu Pohang, Korea
– Phone :	607 254 3339	82-54-279-2130
– Fax :	607 255 4137	82-54-279-3399

Period of Performance: 05/27/2010 – 05/26/2013

**Note: NBIT is a collaborative research program with Korean scientists. Therefore, please include in the report your Korean partner's NBIT research results. Please clearly identify the research that was conducted by the Korean team and U.S. team.*

***Also note that AOARD is required to submit the final report to the Defense Technical Information Center (DTIC), which is open to the public.*

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
26 AUG 2013	**Final**	**27-05-2010 to 25-05-2013**

4. TITLE AND SUBTITLE
Meso-size Effect from Self-assembled carbon structures and their device applications (NBIT Phase II)

5a. CONTRACT NUMBER
FA23861014072

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Jiwoong Park

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Cornell University,B50A Baker Laboratory,Ithaca, NY 14853,United States,NY,14853

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD, UNIT 45002, APO, AP, 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-104072

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Despite remarkable developments in the field of carbon nanomaterials, our ability to control and assemble these materials in the meso-size scale is still limited, a problem made more difficult by the lack of imaging tools with necessary resolution and speed. Therefore, there have been constant needs for the development of powerful new imaging and spectroscopy tools. Our main research achievement is the development of new imaging techniques for better mesoscale control of the growth and assembly of carbon nanotubes and graphene, one- and two-dimensional sp2 carbon nanostructures. More specifically, we have developed two new optical imaging techniques, widefield Raman imaging and DUV-Vis-IR hyperspectral imaging, for direct, high-throughput imaging of these 1D and 2D materials. Our new techniques have allowed the investigation of novel physical phenomena, including the angle dependent optical resonances in twisted bilayer graphene. These well-defined carbon nanostructures and their mesoscale assembly will lead to exciting new device applications in energy conversion and energy transfer.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**7**	

Abstract: Despite remarkable developments in the field of carbon nanomaterials, our ability to control and assemble these materials in the meso-size scale is still limited, a problem made more difficult by the lack of imaging tools with necessary resolution and speed. Therefore, there have been constant needs for the development of powerful new imaging and spectroscopy tools. Our main research achievement is the development of new imaging techniques for better mesoscale control of the growth and assembly of carbon nanotubes and graphene, one- and two-dimensional sp^2 carbon nanostructures. More specifically, we have developed two new optical imaging techniques, widefield Raman imaging and DUV-Vis-IR hyperspectral imaging, for direct, high-throughput imaging of these 1D and 2D materials. Our new techniques have allowed the investigation of novel physical phenomena, including the angle dependent optical resonances in twisted bilayer graphene. These well-defined carbon nanostructures and their mesoscale assembly will lead to exciting new device applications in energy conversion and energy transfer.

Introduction: Nanoscale and meso-scale materials are different from macroscopic systems because their properties are highly sensitive to small structural and chemical changes. While this provides exciting advantages through the tuning of their electrical, optical, mechanical and thermal properties, this also makes it difficult to produce mesoscale structures with uniform properties. Overcoming this problem would require new approaches that improve our capabilities in both their synthesis/assembly and characterization. To this end, we need new characterization methods with high spatial, temporal and energy resolution that allow interrogation of the interplay between the structure and chemical/physical properties of mesoscale materials.

Over the past three years, our main research achievement has been ***the development of new imaging techniques*** for better mesosclae control of the growth and assembly of carbon nanotubes and graphene, one- and two-dimensional sp^2 carbon nanostructures. (Fig 1) Despite remarkable developments in this field, our ability to control their heterogeneity is still limited, a problem made more difficult by the lack of imaging tools with necessary resolution and speed. This problem can be overcome by developing powerful new imaging and spectroscopy tools. In addition, one may combine optical and electron microscopy techniques in order to investigate various structure-property relationships.

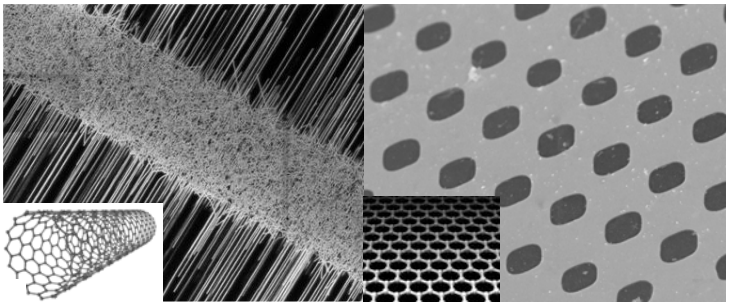

FIGURE 1. Carbon nanotube and graphene (left) Scanning electron microscope (SEM) image of CNTs on quarts. (right) SEM image of suspended graphene array

The two new optical imaging techniques, ***widefield Raman imaging*** and ***DUV-Vis-IR hyperspectral imaging***, enable direct, high-throughput imaging of 1D and 2D materials. Significant accomplishments of our work in this area now include rapid and parallel Raman imaging of many individual carbon nanotubes on a substrate, chemical identification of graphene versus hexagonal boron nitride in their lateral heterostructures and the first comprehensive understanding of the interlayer coupling in twisted bilayer graphene. These studies provided new insights that allow better control of the growth and assembly of carbon nanotubes, graphene, and other 2D materials, and they will lead to studies of intertube and interlayer coupling under physical and chemical regimes previously unavailable. Furthermore, these well-defined carbon nanostructures and their mesoscale assembly will lead to exciting new device applications in energy conversion and

energy transfer. Over the last three years, our joint research results have appeared in many reputable journals (more than 12 total), including *Nano Letters* (2), *ACS Nano* (2) and *NPG Asia Materials* (2). Our work also resulted in two provisional patent filings.

Experiments and Results:

Korean Team (Choi group)

As witnessed by quantum size effect, the intrinsic properties of chemical elements in bulk or molecular scale become variant depending on the sizes and shapes. In the past three years, we have investigated three examples of self-crystallized structures exhibiting optical, optoelectrical and chemical properties that are unprecedented when the component unit molecules of the self-crystallized structures are present in ensemble states. These include 1) remarkably increased photoluminescence (PL) from C_{70} cube crystals, 2) crystal plane-dependent PL activity and electrical photoresponse from pentacene 1D disks and 2D wires, and 3) dramatic increase of solubility in water of zinc phthalocyanine (ZnPc) nanowires. The details about the structure-property correlations derived from aforementioned examples are discussed in the following publications.

[1] Park, J. E.; Hong, M.; Son, M.; Choi, H. C.* "Crystal Plane-Dependent Photoluminescence Activity of Pentacene 1D Wire and 2D Disk Crystals." ***Angew. Chem. Int. Ed.*** 2012, *51*, 6383-6388.

[2] Moon, H. K.; Son, M.; Park, J. E.; Yoon, S. M.; Lee, S. H.; Choi, H. C.* "Significant increase in the water dispersibility of zinc phthalocyanine nanowires and its application in cancer phototherapy" ***NPG Asia Mater.*** 2012, *4*, 1-8.

[3] Lim, H.; Song, H. J.; Son, M.; Baik, J. Y.; Shin, H. –J.; Choi, H. C.* " The unique photoemission from single-layer graphene on SiO_2 layer by substrate charging effect." ***Chem. Commun.*** 2011, *47*, 8608-8610.

US Team (Park group)

Below we describe three major experiments that have been supported by the current AOARD funding. These results were published in the following three journal papers:

[1] R. W. Havener, S.Y. Ju, L. Brown, Z. Wang, M. Wojcik, C. S. Ruiz-Vargas, and J. Park, "High-Throughput Graphene Imaging on Arbitrary Substrates with Widefield Raman Spectroscopy," ***ACS Nano*** 6, 373 (2012).

[2] R. W. Havener, H. Zhuang, L. Brown, R. Hennig, and J. Park, "Angle-Resolved Raman Imaging of Interlayer Rotations and Interactions in Twisted Bilayer Graphene", ***Nano Letters***, 12, 3162-3167 (2012).

[3] R. W. Havener, C.-J. Kim, L. Brown, J. W. Kevek, J. D. Sleppy, P. L. McEuen, and J. Park, "Hyperspectral imaging of structure and composition in atomically thin heterostructures", ***Nano Letters***, 13, 3942-3946 (2013).

Widefield Raman Imaging. Laser-based imaging and characterization of individual nanostructures possess significant advantages over other imaging techniques, such as scanning probe microscopy and electron microscopy, and they will provide new characterization tools for exploring meso-size effects in carbon structures.

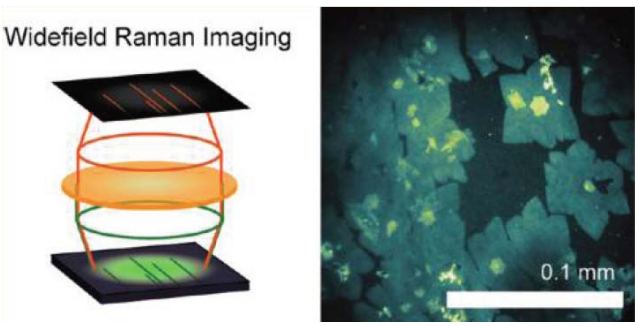

FIGURE 2. Widefield Raman imaging on graphene.

We developed a spectrally-resolved widefield Raman imaging (WRI) technique (Fig 2) that images carbon nanotubes and graphene with a speed three orders of magnitude faster than the conventional micro-Raman technique. We combined widefield illumination from an intense (3 W) laser beam with tunable optical filters to image the Raman-scattered bands (D, G, 2D) unique to carbon nanotubes and graphene, providing a diffraction limited image for a large field of view. This enables fast identification of individual carbon nanotubes in seconds, after which high-resolution Raman spectra can be obtained for a region of interest using an imaging spectrometer. The widefield geometry enables large-scale studies of various carbon structures, while providing comparable spectral information to that obtainable with micro-Raman imaging. We expect that WRI will be a powerful experimental technique for both practical and fundamental studies of carbon structures. Using this technique we have also resolved parallel nanotubes at the optical diffraction limit. While only a portion of all nanotubes are visible under this setup using a single excitation wavelength (532 nm, > 2W), continuous tuning of the excitation laser wavelength would enable hyperspectral Raman imaging of multiple CNTs on non-transparent substrate.

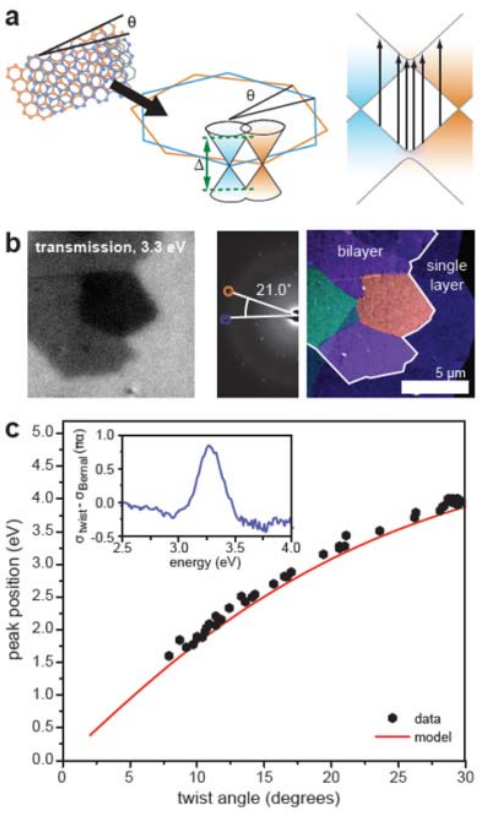

FIGURE 3. **a**. Twisted BLG and a new optical transition **b**. Optical transmission image (left) on resonance vs darkfield TEM image (right) **c**. Resonance energy vs twist angle.

Structure Dependent Optical Conductivities of Bilayer Graphene. The rapidly growing library of isolated two-dimensional materials with diverse electronic and optical properties, and recent advances allowing precise stacking and lateral stitching of these materials, have opened the door for fabrication of atomically thin heterostructure devices with complex, tailorable functionality. In particular, the potential for coupling between stacked atomically thin materials, separated by less than a nanometer across hundreds of square microns or more, is enormous. Despite this, very little is known about whether these heterostructures could possess unique and useful optical or electronic characteristics not found in either isolated layer.

One of the simplest layered structures is twisted bilayer graphene (tBLG) (FIG 3a), and we have characterized optical signatures of tBLG not found in single-layer graphene, indicating that interlayer interactions play an important role in this material. The absorption spectrum of single-layer graphene is relatively featureless, with nearly constant absorption for NIR and visible wavelengths, and a broad, asymmetric absorption peak at 4.6 eV due to graphene's saddle point (M-point) exciton. However, tBLG exhibits an additional absorption peak whose energy varies with twist angle from the infrared (low angles) to the deep ultraviolet (30°). The coupling between the layers enables new optical transitions where the Dirac cones from each layer intersect in momentum space; the bands from each layer run parallel to each other (FIG 3a), creating a large joint density of states for these new transitions.

Because of the broad spectral range of these features, full optical characterization of twisted bilayer graphene required unique, broadband optics. For these experiments, we built a

new **DUV-VIS-IR hyperspectral microscope** with a monochromated 1000W xenon lamp, allowing imaging and spectroscopy from <1.5 to >6.2 eV. Combined with darkfield transmission electron microscopy (DF-TEM), which enables imaging of the crystalline orientation of individual graphene grains, we have studied the optical absorption of tBLG as a function of twist angle (FIG 3b,c). The position of the first absorption peak vs. angle is well-described by a non-interacting tight binding model. We also observe a variety of other interesting features at higher energies, including a marked suppression of graphene's 4.6 eV absorption peak for the highest twist angles. The origin of these features is currently unknown, but may point to further interactions between the two layers.

Imaging and Spectroscopy of Boron Nitride. A large wavelength range is essential for studying arbitrary two-dimensional materials, from metals like graphene to insulators like hexagonal boron nitride (*h*-BN), in complex geometries. While we have already discussed interesting physics and potential applications for the case of twisted bilayer graphene (see above), this is only the beginning of the complex structures we could build with a larger set of starting materials. For this, we have made significant progress, performing quantitative, spatially-resolved spectroscopy of both graphene and *h*-BN with our hyperspectral microscope (FIG 4). This clearly demonstrates that the high tunability of the source in our DUV-Vis-IR hyperspectral imaging microscope ensures that we capture the key spectroscopic features of both materials.

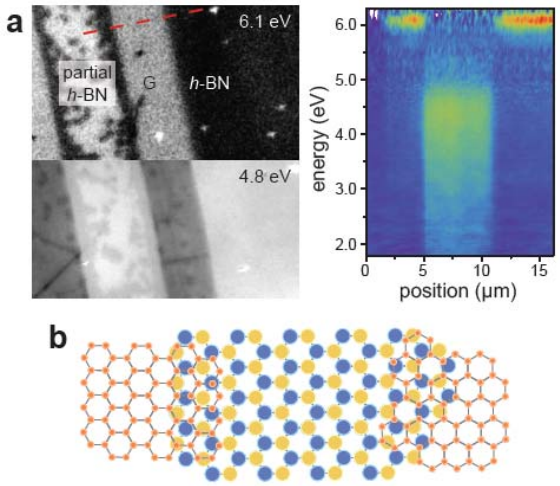

FIGURE 4. **a**. Transmission imaging of graphene(G) and boron nitride (BN) heterostructures at 6.1eV and 4.8eV (right) spectral map along the red dashed line **b**. Structural schematic of the heterojunction.

Discussion: During the current grant period, we have developed novel optical approaches that enable us to image individual CNTs using new techniques and geometries for wide-field Raman, and absorption imaging spectroscopy. We also developed new imaging methods for high throughput, broadband imaging and spectroscopy of atomically thin materials, including graphene and hexagonal boron nitride. However, our current illumination sources enabling these measurements are limited to discrete line sources, low-power supercontinuum 'white-light' emission, and incoherent arc lamps. To continue our developments in high-throughput spectral imaging, a fundamental roadblock has been

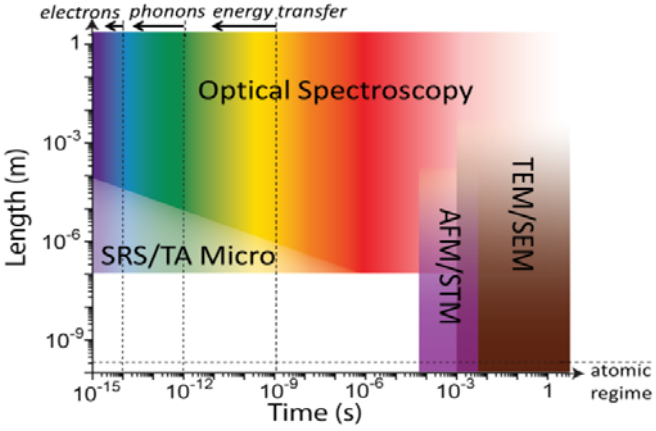

FIGURE 5. To resolve critical processes at the nanoscale such as energy transfer and electron-phonon interaction we require the ability to resolve both the *ultrasmall* (<1 μm) and *ultrafast* (<1 ns). Few techniques meet both criteria.

obtaining an appropriately versatile light source which meets our basic requirements of (*i.*) broad (UV to NIR) continuous wavelength tunability and (*ii*.) high laser power to enable efficient wide-field imaging and Raman spectroscopy. A powerful laser setup, such as the Coherent Chameleon Ultra II + APE automated optical parametric oscillator (OPO) would allow us to overcome this roadblock. In addition, such high-power tunable laser will enable fundamentally new techniques for nanomaterial imaging while providing new information at both the *ultrasmall* and *ultrafast*. (See FIG 5)

We find novel applications of tBLG for optoelectronic and photovoltaic devices. For instance, an applied electric field would break the symmetry between the layers, and potentially enable optical pumping of electrons from one layer to the other at a specific wavelength determined by twist angle. Analogous to carbon nanotubes with varying chiralities, tBLG with various angles could serve as the active component in highly tunable photovoltaic devices made from a single starting material. Excitons, such as those found in single-layer graphene at high energies, may have significant effects on the energy and lifetime of these excited states. Understanding the nature and dynamics of excitons under the presence of interlayer interaction in graphene, as well as other two-dimensional materials, requires new characterization tools ideally provided by ultrafast optical techniques.

Finally, *h*-BN is typically considered to be an inert substrate for graphene electronics, but the interactions between these two materials would become apparent at higher energies, where screening from the graphene layer is expected to redshift the *h*-BN exciton. *h*-BN could also be used as a spacer to tune the distance, and therefore the interaction strength, between twisted graphene or other layered materials in controllable increments of ~0.3 nm. As in the case of twisted bilayer graphene, the momentum space interaction between carriers in arbitrary two-dimensional materials could have a significant dependence on the relative angle between the layers. This additional degree of freedom needs to be understood for controllable device fabrication. Also of interest are the dynamics of charge transfer and photovoltaics in semiconducting atomically thin materials, such as MoS_2, $MoSe_2$, or BCN, with varying band gaps. Understanding the fundamental properties of these materials will be essential as an additional building block for active electronic and optoelectronic devices.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a) papers published in peer-reviewed journals:

US team:

[1] R. W. Havener, C.-J. Kim, L. Brown, J. W. Kevek, J. D. Sleppy, P. L. McEuen, and J. Park, “Hyperspectral imaging of structure and composition in atomically thin heterostructures”, ***Nano Letters***, 13, 3942-3946 (2013).

[2] R. W. Havener, H. Zhuang, L. Brown, R. Hennig, and J. Park, “Angle-Resolved Raman Imaging of Interlayer Rotations and Interactions in Twisted Bilayer Graphene”, ***Nano Letters***, 12, 3162-3167 (2012).

[3] R. W. Havener, S.Y. Ju, L. Brown, Z. Wang, M. Wojcik, C. S. Ruiz-Vargas, and J. Park, "High-Throughput Graphene Imaging on Arbitrary Substrates with Widefield Raman Spectroscopy," ***ACS Nano*** 6, 373 (2012).

[4] J. M. Kinder, J. Park, and G. K.-L. Chan, "Uniform Peak Optical Conductivity in Single-Walled Carbon Nanotubes," ***Phys. Rev. B***. 84, 125428 (2011).

[5] S. Chen, L. Brown, M. Levendorf, W. Cai, S.-Y. Ju, J. Edgeworth, X. Li, C. Magnuson, A. Velamakanni, R. Piner, J. Park, and R. Ruoff, “One-atom-thick

protection coating: oxidation and corrosion resistance of graphene-coated metal," ***ACS Nano*** 5, 1321-1327 (2011).

Korean team:

[6] Kim, H.; Son, Y.; Park, C.; Cho, J.; Choi, H. C.*, "Catalyst-free Direct Growth of a Single to a Few Layers of Graphene on a Germanium Nanowire for the Anode Material of a Lithium Battery" ***Angew. Chem. Int. Ed.*** 2013, *52*, 5997-6001.

[7] Park, J. E.; Hong, M.; Son, M.; Choi, H. C.* "Crystal Plane-Dependent Photoluminescence Activity of Pentacene 1D Wire and 2D Disk Crystals." ***Angew. Chem. Int. Ed.*** 2012, *51*, 6383-6388.

[8] Moon, H. K.; Son, M.; Park, J. E.; Yoon, S. M.; Lee, S. H. ; Choi, H. C.* "Significant increase in the water dispersibility of zinc phthalocyanine nanowires and its application in cancer phototherapy" ***NPG Asia Mater.*** 2012, *4*, 1-8.

[9] Lim, H.; Song, H. J.; Son, M.; Baik, J. Y.; Shin, H. –J.; Choi, H. C.* " The unique photoemission from single-layer graphene on SiO_2 layer by substrate charging effect." ***Chem. Commun.*** 2011, *47*, 8608-8610.

[10] Son, M.; Lim, H.; Hong, M.; Choi, H. C. "Direct Growth of Graphene Pad on Exfoliated Hexagonal Boron Nitride Surface." ***Nanoscale***, 2011, *3*, 3089-3093.

Joint publications:

[11] H. J. Song, M. Son, C. Park, H. Lim, M. P. Levendorf, A. W. Tsen, J. Park, and H. C. Choi, "Large Scale Metal-free Synthesis of Graphene on Sapphire and Transfer-free Device Fabrication", ***Nanoscale***, 4, 3050-3054 (2012).

[12] R. Havener, W. Tsen, H. C. Choi, and J. Park, "Laser-based imaging of individual carbon nanostructures," (invited review paper) ***NPG Asia Materials*** 3, 91-99 (2011).

b) papers published in peer-reviewed conference proceedings,
c) papers published in non-peer-reviewed journals and conference proceedings,
d) conference presentations without papers,
e) manuscripts submitted but not yet published, and

f) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

Our work on the development of the widefield Raman technique also resulted in a new Korea-US industrial collaboration that includes Samsung Techwin as the industrial partner. We have collaborated on developing a Raman based test bench that can be integrated with the current large scale CVD setup for graphene production in 2012.

Attachments: Publications a), b) and c) listed above if possible.

DD882: As a separate document, please complete and sign the inventions disclosure form.